PARAMAGNETIC SUSCEPTIBILITIES OF THE $3d^n$ OCTAHEDRAL COMPLEXES

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Received August 24, 1968

ABSTRACT. In the Octahedral complexes of the transition metal ions the temperature independent high-frequency contribution to paramagne susceptibilly χ'_h coming from the first excited configuration has been estimated. This contribution must be differentiated from the usual high-frequency contribution coming from the ground configuration denoted by χ_h. The magnitude of this contribution depending on a particular ion and a particular complex varies roughly from 1% to 9% of the room temperature susceptibility value and is thus quite significant. This means that the magnitudes of the crystal field parametor Δ, the spin-orbit coupling constant in the crystal ζ etc. usually obtained from the ground configuration alone will be altered somewhat in the temperature range 200°K to 300°K when this additional contribution is also taken into account.

INTRODUCTION

During the past decade there has been a good amount of work on the paramzgnetic susceptibilities of the complexes of the transition metal ions (Uryu, 1956; Chakravarty, 1959; Bose *et al* 1960, 1961, 1962). But in all these investigations the ground configuration has only been taken into consideration on the assumption that the excited configurations will not contribute significantly because of their large energy separations from the ground configuration. It is the purpose of this paper to show that actually it is not so. The second order temperature independent Van Vleck susceptibility coming from the first excited configuration (first excited configuration corresponds to one electron excitation from the ground configuration) is quite appreciable in the type of complexes under consideration. A preliminary theoretical account of this contribution has been already given by Griffith (1961). But his interest was mainly confined with showing roughly the effect of this contribution to the Bohr magneton number μ_{eff}. But it is easy to realise that the μ_{eff} would be rather insensitive to small alteration of the susceptibility values due to the contribution coming from the excited fonfiguration. We have, however, calculated this contribution for the individual ions Ti^{3+} through Cu^{2+} and show that it is roughly between 1% and 9% of the room temperature susceptibility value. In our calculations we have assumed the hydrated complexes of the transition metal ions to be approximately octahedral in symmetry. The reason is that the slight departure of the crystalline electric

field from octahedral symmetry will not alter the magnitudes of this contribution very much so that our conclusions will be correct to a very high degree of approximation. This assumption, on the other hand, reduces the labour appreciably.

THEORETICAL ASPECTS

For the theoretical aspects one should consult Griffiths (1961) and therefore we should mention here only the important points. Since the Hamiltonian for for the magnetic perturbation involves the orbital angular momentum $\vec{L}$ and because $\vec{L}$ is one-electron operator, the matrix element of the magnetic Hamiltonian is non-vanishing between the terms of the ground and first excited configuration. But since the orbital angular momentum $\vec{L}$ of the free ions gets somewhat reduced when the ions form the octahedral complexes we must take this fact also into consideration. We denote this orbital reduction factor by k. The value of this reduction factor has been assumed to be 0.9 (Owen and Thornley, 1966). We believe this is a reasonable value in the type of complexes we are considering. It should also be noted that we have calculated this high frequency contribution χ'_h in the strong field approximation (Ballhausen, 1962). The final expression which we have used can be shown to be

$$\chi_h = -\frac{2N\beta^2}{3} \sum \frac{\langle \psi_n | k\vec{L} | \psi_0 \rangle}{E_n - E_0} \qquad \ldots (1)$$

where ψ_0 is the ground state belonging to the configuration $t^m_{2g}\, e_g^n$ and ψ_n are the spin-allowed excited states belonging to the configuration $t_{2g}^{m-1} e_g^{n+1}$. Other configurations will have no effect because L is a one-electron operator. We write χ'_h to differentiate it from the usual high frequency contribution coming from the ground configuration which is customarily denoted by χ_h. $E_n - E_0$ is the energy separation between the ground and the excited states. The energy separations have been found from the experimental optical absorption spectra of these complexes (see the references at the end of table 1). The strong field wave functions in the crystal field of octahedral symmetry have been derived by us using the methods of Tanabe and Sugano (1954) which we do not present here. The correctness of the wave functions was checked by finding the electrostatic energy matrix elements and comparing them with Tanabe and Sugano matrices. χ'_h calculated in this way are presented in table 1 and are compared with the room temperature susceptibility values for the ionic complexes. The calculation for the $3d^5$ system has no been done because the ground state of this system is a $^6A_1$ state and there is no sextet present in the first excited configuration.

Config.	Ion	Complexes	Transition (g→g)	$\lvert\langle\lvert L\rvert\rangle\rvert^2$	Energy differences	(A) χ_h' Calculated	(B) χ Experimental at 300°K	$\frac{\chi_h'}{\chi}$ in %
$3d^1$	Ti^{3+}	$Ti(H_2O)_6^{3+}$	$^2T_2 \rightarrow {}^2E$	12	20300[a]	84.48	1188[j]	7.11
$3d^2$	V^{3+}	$V(H_2O)_6^{3+}$	$^3T_1 \rightarrow {}^3T_1(t_2e)$ $\rightarrow {}^3T_2(t_2e)$	6 18	25200[b] 17100[b]	181.76	3062[l]	5.93
$3d^3$	V^{2+}	$V(H_2O)_6^{2+}$	$^4A_2 \rightarrow {}^4T_2(t_2^2e)$	12	11800[d]	153.37	5510[n]	2.73
	Cr^{3+}	$Cr(H_2O)_6^{3+}$	$^4A_2 \rightarrow {}^4T_2$	12	17400[e]	97.20	5510[n]	1.76
$3d^4$	Cr^{2+}	$Cr(H_2O)_6^{2+}$	$^5E(t_2^3e) \rightarrow {}^5T_2(r_2^2e^2)$	12	14000[b]	120.69	8740[n]	1.38
	Mn^{3+}	$CsMn(SO_4)_2.12H_2O$	$^5E \rightarrow {}^5T_2$	12	21000[f]	81.00	8740[n]	0.92
$3d^6$	Fe^{2+}	$Fe(H_2O)_6^{2+}$	$^5T_2(t_2^4e^2) \rightarrow {}^5E(t_2^3e^3)$	12	10400[g]	163.37	12360[k]	1.32
$3d^7$	Co^{2+}	$Co(H_2O)_6^{2+}$	$^4T_1(t_2^5e^2) \rightarrow {}^4T_2(t_2^4e^3)$ $\rightarrow {}^4T_1(t_2^4e^3)$	18 6	8200[h] 20000[e]	351.46	10250[m]	3.40
$3d^8$	Ni^{2+}	$Ni(H_2O)_6^{2+}$	$^3A_2(t_2^6e^2) \rightarrow {}^3T_2(r\,e^3)$	12	8500[i]	198.85	4693[k]	4.23
$3d^9$	Cu^{2+}	$Cu(H_2O)_6^{2+}$	$^2E(t_2^6e^3) \rightarrow {}^2T_2(t_2^5e^4)$	12	126000	134.46	1410[n]	9.53
		$CuSO_4.5H_2O$	$^2E \rightarrow {}^2T_2$	12	13000	129.60	1410[n]	9.19

(a) Hartmann *et al*, 1956; (b) Hartmann and Furlani 1956; (c) Lone 1957; (d) Holmes and McClure 1956; (e) Jorgensen, 1954; (f) Hartmann and Schlafer, 1951; (g) Jorgensen 1954; (h) Dreisch and Trommer, 1937; (i) Jorgensen, 1955; (j) Bose, *et al*, 1960 (k) Bose, *et al* 1961; (l) Chatterjee, 1962; (m) Bose *et al* 1963; (n) Griffith, 1961.

DISCUSSION

We have calculated χ'_h for the octahedral complexes of the $3d^n$ transition metal ions. The same calculation can also be done for the tetrahedral complexes and in these cases the magnitudes of χ'_h would be even bigger because the energy separation $E_n - E_0$ appearing in the denominator of eqn. (1) is usually much less than that in the octahedral complexes. It is evident from table 1 that at the room temperature the contribution of χ'_h to the ground configuration total paramagnetic susceptibility varies from 1% to 9% depending on the particular complex. This contribution from the excited configuration will alter the crystalline field parameters, the effective Landé factors as well as the spin-orbit coupling parameter somewhat appreciably in the temperature range $200°K - 300°K$ in the manner explained below.

In calculating the susceptibility expression in the ground configuration, the Hamiltonian that is usually considered is given by (Abragam and Pryce, 1951)

$$H = H_{Free\ ion} + V_{Cubic} + \Delta(1 - l'^2_z) - \alpha\zeta l'_z S_z - \alpha'\zeta(l'_x S_x + l'_y S_y) + \beta(\vec{L} + 2\vec{S}).\vec{H} \qquad (2)$$

where V_{cubic} is the crystalline electric field potential of octahedral symmetry, Δ is the strength of the crystal field of tetragonal or trigonal symmetry, $-\alpha$ and α' are the effective Landé factors in the axial and perpendicular directions, l'_z is the z-component of the effective orbital angular momentum, ζ is the spin-orbit coupling parameter in the crystal. ζ, Δ, α and α' are the parameters first introduced by Abragam and Pryce (1951) for the orbitality degenerate ground states such as in $V^{3+}(3d^2)$, $Fe^{2+}(3d^6)$ and $Co^{2+}(3d^7)$. Now, as soon as the expressions for the susceptibility, involving the parameters Δ, ζ, α and α' are obtained by using the above Hamiltonian, one makes a trial and error calculation to fit the theory with the experimental susceptibility curve at different temperatures. In this way one gets the magnitudes of the above mentioned parameters. The fitting of the data are done in most cases within 1% accuracy. It is very important to note that the contribution from the excited configuration which varies from 1% to 9% in different cases must be taken into consideration along with the major contribution from the ground configuration before interpreting the susceptibility vs. temperature curve. As a result, all the parameters appearing in the above Hamiltonian will have different magnitudes compared with those calculated without considering the said contributions. It is important to note that the magnitudes of the parameters will differ significantly in the range 100°K to 300°K but not appreciably at temperatures below 100°K because the magnitude of susceptibility goes on increasing as the temperature decreases whereas

this high-frequency contribution from the excited configuration is temperature independent and therefore remains the same at all temperatures.

ACKNOWLEDGEMENT

We are grateful to Professor A. K. Saha for his kind interest in this work.

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